Surface and edge energy of electron gas in nanocrystals.

M. V. Entin and M. M. Mahmoodian

Institute of Semiconductor Physics, Siberian Branch of the RAS,
630090 Novosibirsk, Russia

Abstract. The energy of a many-electrons nanoparticle depends on its form via the surface and edge contributions to the thermodynamic functions. The surface energy of free electron gas is found for a semiconductor with the Dirac spectrum. The edge energy of electron gas is calculated for quadratic energy spectrum of electrons without and with anisotropy. We find also spin-orbit corrections to the surface energy, which behave like the inverse square of crystal size.

Quantum dots with the large number of electrons are intermediate objects between the quantum and the classical limits. On the one hand, their sizes are large compared with the electron wavelength. On the other hand, the transport and thermodynamic properties of the system are affected by the quantization of the electron states.

In the degenerated electron system the surface contribution to the thermodynamics of small particles is determined by the small ratio of the Fermi wavelength of the electron $1/k_F$ to the particle size L. The presence of the surface leads to the regular corrections in powers of this parameter to the chemical potential of electrons [1].

The surface contributions to the energy of the electron gas lead to the different physical effects. In particular, they affect the surface tension in small particles and, consequently, their equilibrium form. Establishment of the equilibrium between the electron gas in microparticles with different size or form is accompanied by their spontaneous charging [1]. As was shown in [2], owing to charge discreteness, the chemical potentials in microparticles are not completely equalized. As a result, the system of metal granules becomes a gapless insulator (the gapless Hubbard insulator).

Aside from the surface contribution to the energy, in facetted nanocrystals there are contributions caused by their edges and vertexes [3]. The goal of the present report is the study of surface and edge energies of three- and two-dimensional facetted nanocrystals.

Edge contribution to the energy in the free electron model

Here we consider two or three-dimensional gas of free electrons, bounded by an angle $0 < \varphi < \phi, r = \sqrt{x^2 + y^2} < R$ (the dihedral angle in 3D case). The electron wave function ψ satisfies the condition $\psi = 0$ on the angle borders. We search the corrections to the Ω potential at zero temperature, caused by presence of the edge and the boundary. The contribution to the Ω potential from the vicinity $r < r_0$ of the edge $r = 0$ is

$$\Omega = -\int\limits_{0}^{L_z} dz \int\limits_{0}^{r_0} r\,dr \int\limits_{0}^{\phi} d\varphi \sum (\mu - \varepsilon_{n,m} - k_z^2/2m_e)|\psi_{n,m}(z,r,\varphi)|^2 \qquad (1)$$

Here $\varepsilon_{n,m}$ is the energy level of the electron with the main n and the magnetic m quantum numbers, k_z is the momentum along the edge, m_e is the electron effective mass, $\mu =$

$k_F^2/2m_e$ is the chemical potential. The axis z is directed along the edge and L_z is the edge length. In 2D case this variable and corresponding integration should be excluded.

When the radius R of the sector goes to infinity, Ω ceases to depend on the sector size. In the limit $k_F r_0 \gg 1$ Ω yields an asymptotic expansion (3D case):

$$\Omega = \omega_3 L_z \phi r_0^2/2 + \omega_2 L_z r_0 + \omega_1 L_z + o(1). \tag{2}$$

The wave function, satisfying boundary conditions is

$$\psi_{n,m}(z, r, \varphi) = \sqrt{\frac{2\pi k}{\phi R}} \exp(i k_z z) J_\nu(kr) \sin(\nu\varphi), \quad \nu = \frac{\pi m}{\phi}. \tag{3}$$

Using the wave function (3) we find

$$\Omega = \frac{1}{m_e r_0^2} \frac{L_z}{\pi} \int\limits_0^{k_F} dk_z u^4 \int\limits_0^1 x dx [\ln x + \frac{1}{2}(1 - x^2)] \sum_{m=1}^{\infty} J_{\frac{\pi m}{\phi}}^2(ux). \tag{4}$$

Here $u = (k_F^2 - k_z^2)^{1/2} r_0$.

The expansion of (4) in the orders of r_0 at $r_0 \to \infty$ gives ω_3, ω_2 and ω_1. The term $\omega_3 = -k_F^5/15\pi^2 m_e$ is the usual Ω potential of 3D gas. The term $\omega_2 = k_F^4/32\pi m_e$ represents the surface contribution [1,2].

The edge contribution ω_1 yields

$$\omega_1(\phi) = -\frac{k_F^3}{36\pi m_e}\left(\frac{\pi}{\phi} - \frac{\phi}{\pi}\right). \tag{5}$$

Physically the dependence of $\omega_1(\phi)$ is explained by the same factors as the positive sign of the surface contribution to the energy. Zero boundary conditions on the crystal surface deplete the electron gas density in the boundary region. As a result, the size of occupied region decreases that raises the energy of electron gas at the unchangeable number of electrons. The volume of the depletion region grows with the angle that leads to the same change of the energy of electron gas if both crystal volume and surface area don't vary. The change of $\omega_1(\phi)$ sign at $\phi = \pi$ is caused by extracting of the surface part of energy.

Two cases are of special interest. They are the right angle, typical for the facetting of a cubic crystal and the angle $\phi = 2\pi$, corresponding to the rift in the crystal. In these cases $\omega_1(\pi/2) = -k_F^3/24\pi m_e$ and $\omega_1(2\pi) = k_F^3/24\pi m_e$.

By means of (5) the number of electrons in nanocrystal of volume V, the surface area S and edges with angles ϕ_n and lengths L_n is expressed through the chemical potential:

$$N = -\frac{\partial \Omega}{\partial \mu} = \frac{(2m_e\mu)^{\frac{3}{2}} V}{3\pi^2} - \frac{m_e \mu S}{4\pi} + \frac{(2m_e\mu)^{\frac{1}{2}}}{12\pi} \sum_n L_n \left(\frac{\pi}{\phi_n} - \frac{\phi_n}{\pi}\right). \tag{6}$$

The analogous formula is found for the edge energy of a 2D quantum dot with a polygonal border. The angle energy of 2D gas is

$$\omega_1(\phi) = -\frac{k_F^2}{24m_e}\left(\frac{\pi}{\phi} - \frac{\phi}{\pi}\right). \tag{7}$$

Anisotropic electron energy spectrum

The expression for the edge contribution to the energy allows generalization to the case of the anisotropic quadratic-law energy spectrum $\varepsilon(k) = \sum k_i^2/2m_i$. The affine transformation $x_i' = x_i(m_i/m_e)^{1/2}$, where $m_e = (m_1 m_2 m_3)^{1/3}$, converts the Schrödinger equation to isotropic one, for which the previous consideration is valid.

If we establish the dihedral angle by means of the normal vectors $\mathbf{n_1}$ and $\mathbf{n_2}$ to the forming planes, the transformed angle between these planes, entering into previous formulas, is defined by the relation:

$$\cos\phi = \sum_{i=1}^{3} \frac{n_{1i} n_{2i}}{m_i} \left[\sum_{i=1}^{3} \frac{n_{1i}^2}{m_i} \sum_{i=1}^{3} \frac{n_{2i}^2}{m_i} \right]^{-\frac{1}{2}}, \tag{8}$$

and the edge length $L_n = \left[\sum_{i=1}^{3} L_{ni}^2 \right]^{1/2}$ is changed on $\left[\sum_{i=1}^{3} \frac{m_i}{m_e} L_{ni}^2 \right]^{1/2}$.

Dirac model

The Dirac model is the simplest Hamiltonian, describing the energy spectrum of a semiconductor. The most adequately it corresponds to a cubic semiconductor with a non-degenerate central main minimum of the conductivity band and maximum of the valence band. The standard Lattinger model with degenerate maximum of the valence band turns into the Dirac model, if an anisotropy of the band, heavy holes and spin-orbitally splitted band are overlooked. In comparison with the quadratic-law spectrum the Dirac model allows to take into account non-parabolicity of the electron energy spectrum.

The Dirac equation for the spinor component u and v has the form

$$(\varepsilon - m_e c^2)u - c(k\sigma)v = 0, \quad (\varepsilon + m_e c^2)v - c(k\sigma)u = 0. \tag{9}$$

Here ε is the energy of the electron, counted out from the center of the forbidden band with the width $E_g = 2m_e c^2$, σ is the Pauli spin matrix.

Each of the spinor component satisfy the Klein-Gordon equation

$$(\varepsilon^2 - (m_e c^2)^2)u - c^2 k^2 u = 0. \tag{10}$$

The equation (10) transforms into the Schrödinger equation after substitution $(\varepsilon^2 - (m_e c^2)^2) \to 2m_e c^2 E$. If we suppose zero boundary conditions for the large components of the wave function $u = 0$, the agreement with the Schrödinger equation becomes full. Hence, the previous formulae prove correct if we change $\mu = k_F^2/2m_e \to \mu \frac{\mu + E_g}{E_g}$ referring μ to the conduction band bottom.

Spin-orbit induced surface corrections

The spin-orbit interaction is relativistic and usually small effect. Nevertheless, spin-orbit interaction is known [4-5] to be amplified due to confinement by quantum wells. If the width of a well tends to infinity, while the Fermi energy keeps constant, the corrections to the electron spectrum go down inversely as the size. This give rise a new mechanism of the surface corrections to the thermodynamic functions.

Let us consider a planar sample with the width L and the normal z. The spin-orbital correction to the Hamiltonian yields

$$H_{SO} = \lambda \frac{k_z^2}{m_e L} (\sigma_x k_y - \sigma_y k_x) \quad \lambda = \chi \frac{1}{4 m_e^2 c^2}. \tag{11}$$

where χ is some constant of order of unit, depending on the specific surfaces. If the surfaces are equivalent χ vanishes, but in the general case χ is finite.

The Hamiltonian (11) has the energy spectrum $\epsilon(k) = k^2/2m_e \pm \lambda \frac{k_z^2}{m_e L} \sqrt{k_x^2 + k_y^2}$. Substituting this spectrum to Ω potential we find the correction to the number of electrons in the crystal $\Delta N_{SO} = V \lambda^2 L^{-2} k_F^5 / 5\pi^2$. The found correction has, evidently, surface origin. So the order of such correction will be the same in a nanocrystal of any shape with the characteristic size L. This correction turns out to be weaker than the surface correction, proportional to L^{-1}, but may be comparable with the edge corrections.

The numerical calculations of the energy states in many-electron quantum dots are complicated enough problem because of the exponential increasing of the number of energy states, included in the Hamiltonian matrix, with the growing number of electrons. At the same time the considered approach, based on the expanding of thermodynamic quantities in powers of size, allows to get simple estimations without complex calculations.

References

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